

Supporting Information

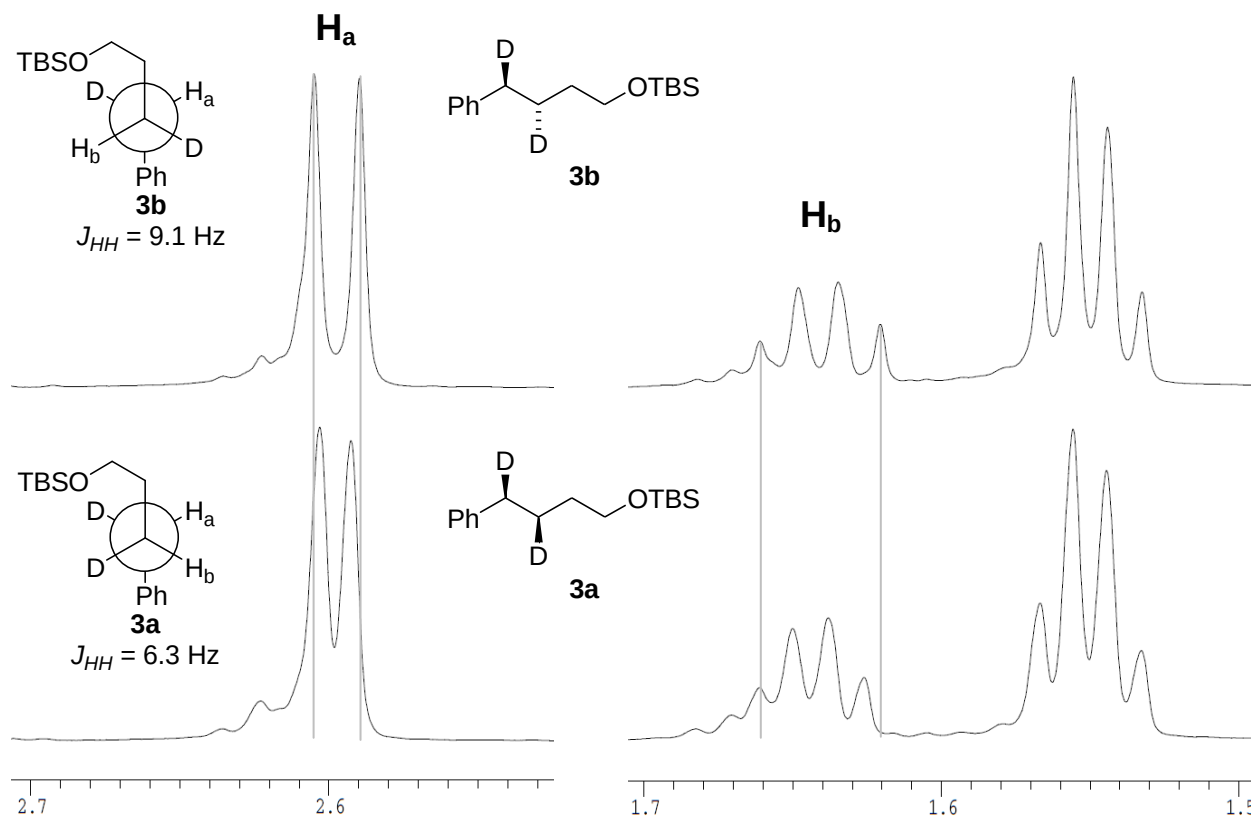
Stereochemistry of Transmetalation of Alkylboranes in Nickel-Catalyzed Alkyl-Alkyl Cross-Coupling Reactions

Buck L. H. Taylor and Elizabeth R. Jarvo*

Department of Chemistry, University of California, Irvine, CA 92697

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Table S1: Variation of amine ligands	S3
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Figure S1: Comparison of ^2H -decoupled ^1H NMR signals for **3a** and **3b**



^1H NMR spectra were recorded at 600 MHz with ^2H -decoupling at 92 MHz, and calibrated to internal TMS. The H_a – H_b coupling constants are measured from the H_a doublet.

Vertical lines were superimposed for comparison of the peaks. Comparison of the H_b quartets indicates that the products were formed as single diastereomers (>95%). The upfield peak of the H_b quartet is resolved, appearing at 1.626 ppm in **3a** and 1.620 ppm in **3b**.

The small upfield shoulders are due to ~5% non-deuterium labeled isotopomers of **3**. See page S15 for a full ^1H spectrum of non-deuterium labeled **SI-3**.

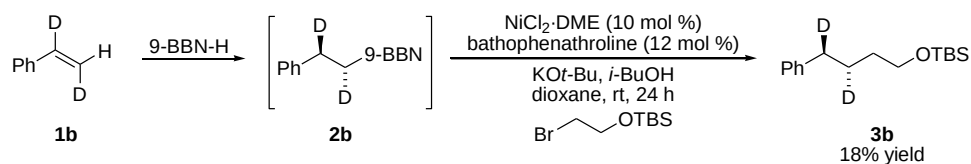
^1H spectra without ^2H -decoupling resulted in similar peaks with comparable H_a – H_b coupling constants (5.6 Hz for **3a** and 9.5 Hz for **3b**). However, the peaks are broadened due to unresolved ^1H – ^2H coupling (~1 Hz). See pages S9–S10 for these spectra.

Table S1: Variation of amine ligands

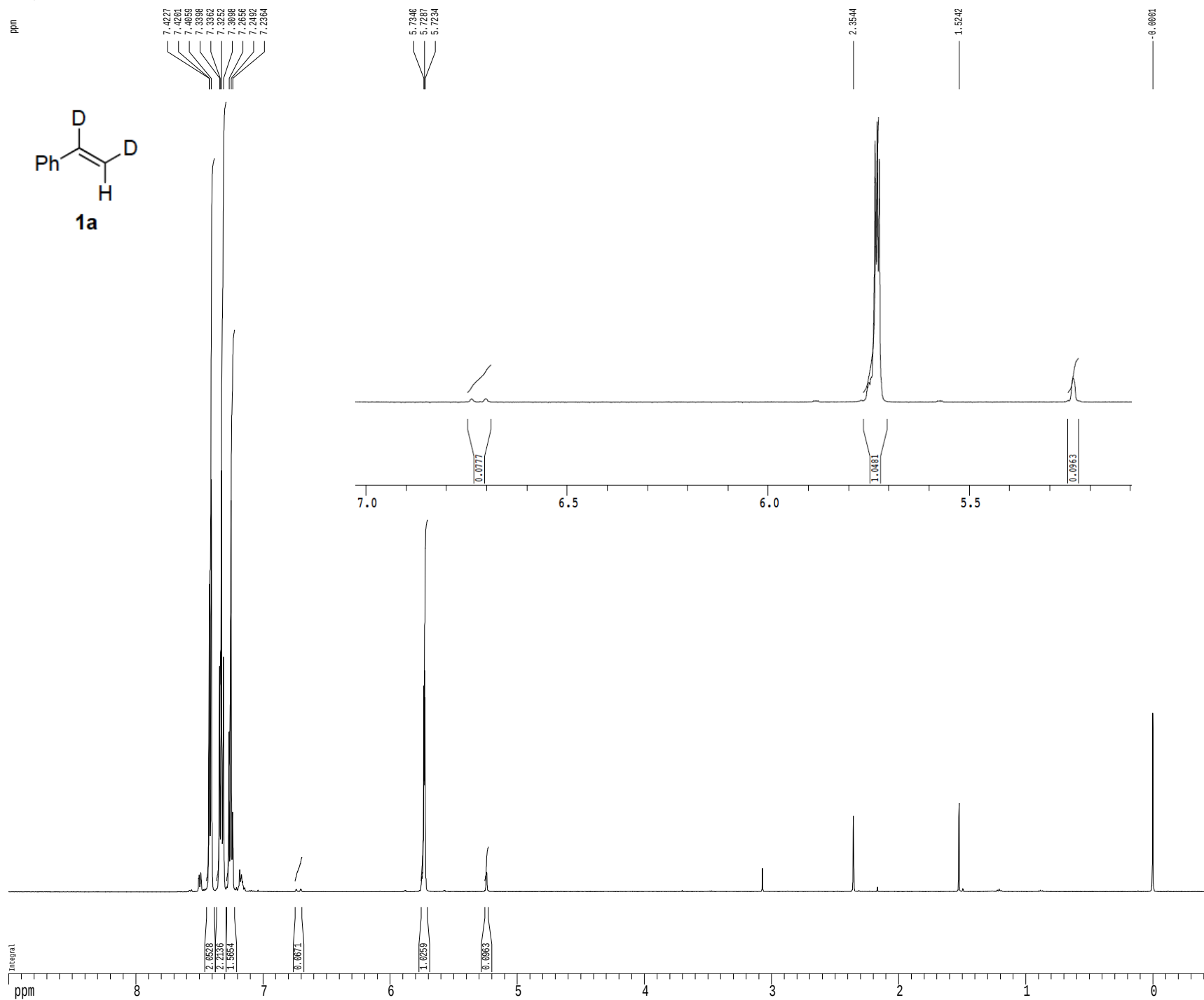
Entry	Ligand	Bromide Remaining ^a	Yield ^a
1		58%	21%
2		75%	15%
3		80%	12%
4		77%	<5%
5		88%	<5%
6		90%	<5%
7		>95%	<5%

^a Yield determined by ¹H NMR by comparison to an internal standard (PhSiMe₃)

Entry 1 was repeated with deuterium-labeled **2b** to afford **3b** as a single diastereomer (>95% as determined by ¹H NMR):



1a
cis-d2-styrene
1H spectrum



Current Data Parameters
 USER taylor
 NAME BLT-2-035-A
 EXPNO 2
 PROCNO 1

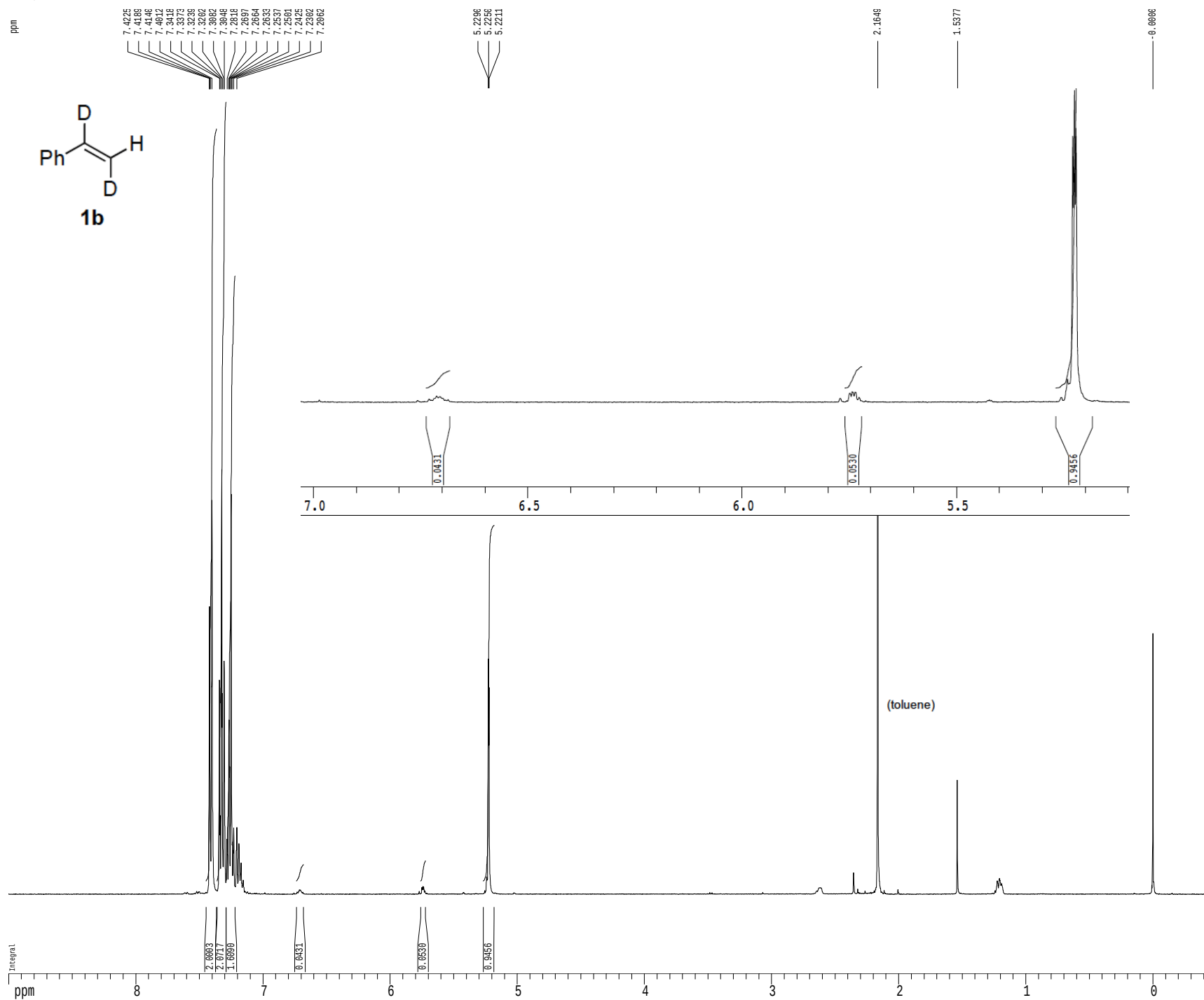
F2 - Acquisition Parameters
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 Time 19.54
 INSTRUM cryo500
 PROBHD 5 mm CPTCI 1H-
 PULPROG zg30
 TD 81728
 SOLVENT CDCl3T
 NS 16
 DS 2
 SWH 8012.820 Hz
 FIDRES 0.098043 Hz
 AQ 5.0998774 sec
 RG 5
 DW 62.400 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.10000000 sec
 MCREST 0.00000000 sec
 MCWRRK 0.01500000 sec

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 P1 7.50 usec
 PL1 1.60 dB
 SF01 500.2235015 MHz

F2 - Processing parameters
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 SF 500.2200365 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 4.00

1D NMR plot parameters
 CX 22.80 cm
 CY 8.00 cm
 F1P 9.000 ppm
 F1 4501.98 Hz
 F2P -0.500 ppm
 F2 -250.11 Hz
 PPMCM 0.41667 ppm/cm
 HZCM 208.42502 Hz/cm

1b
trans-d2-styrene
1H spectrum



Current Data Parameters
USER Taylor
NAME BLT-2-068-A
EXPNO 1
PROCNO 1

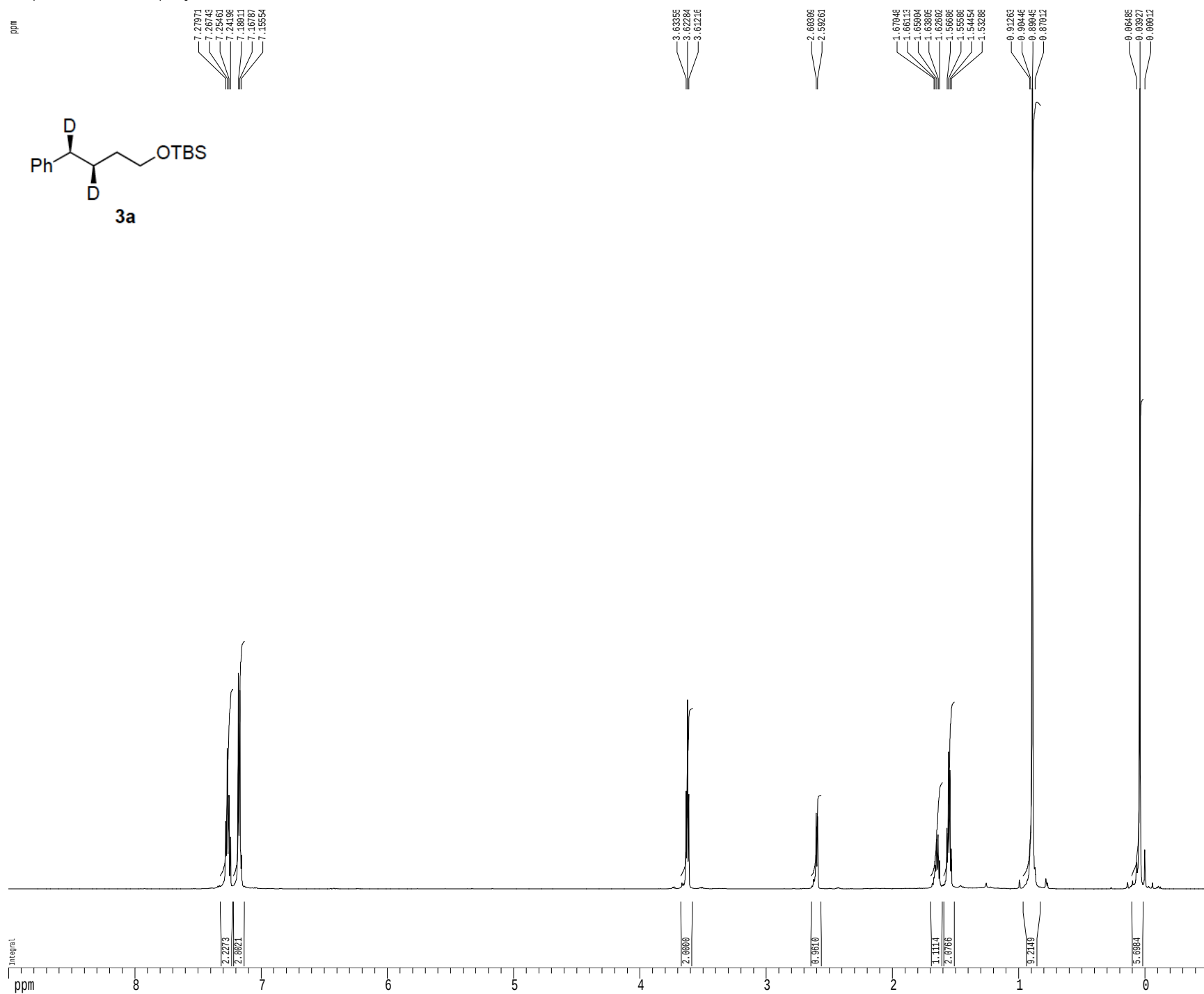
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SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 362
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
SF01 400.1328009 MHz

F2 - Processing parameters
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SF 400.1300257 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.00 cm
CY 30.00 cm
F1P 9.000 ppm
F1 3691.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm

3a
syn-product
1H spectrum with 2H decoupling



Current Data Parameters
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NAME BLT-2-053-A
EXPNO 27
PROCNO 1

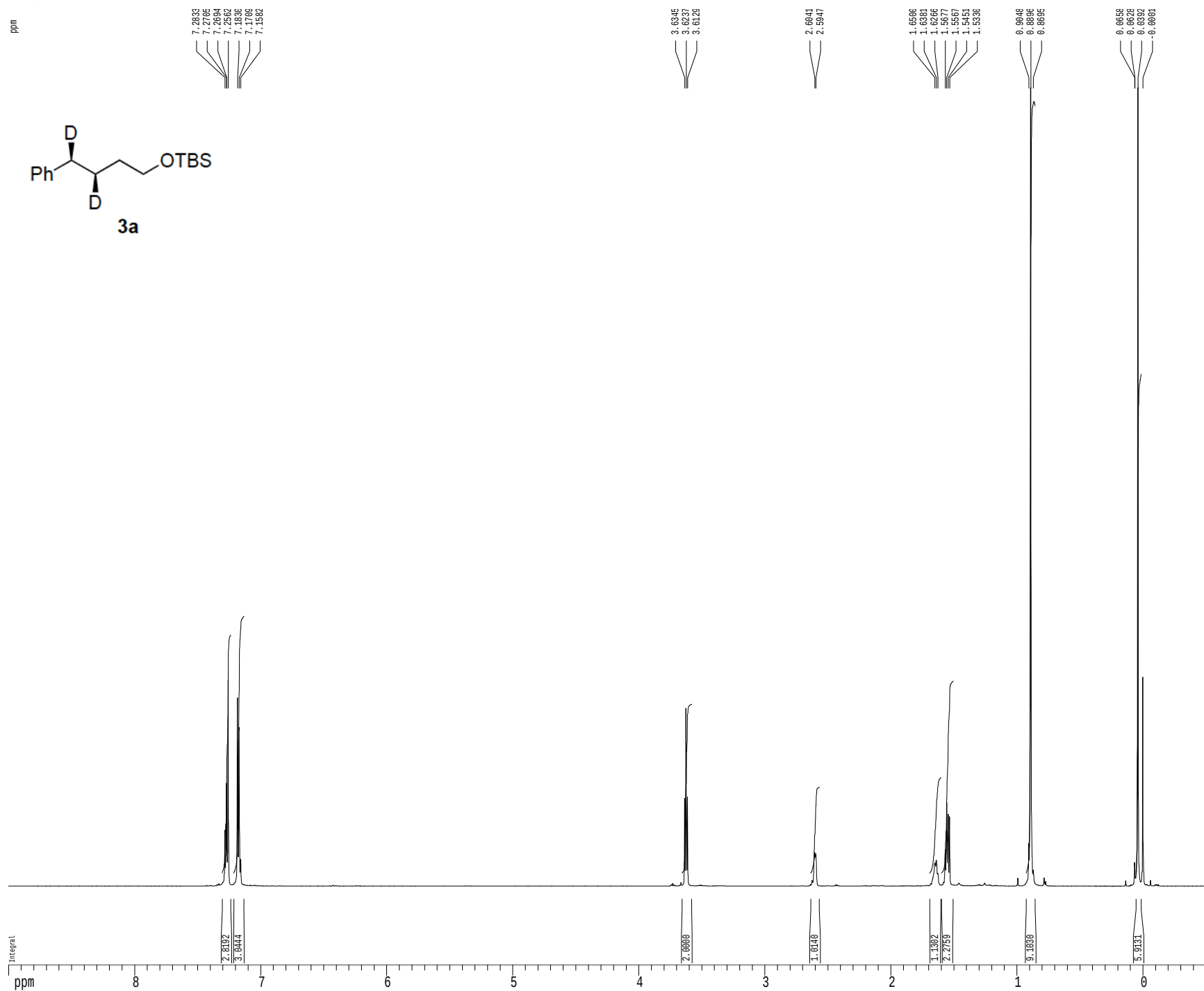
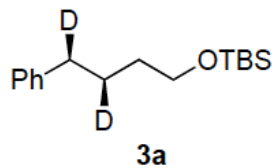
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TD 76786
SOLVENT CDCl3
NS 8
DS 2
SWH 9615.385 Hz
FIDRES 0.125223 Hz
AQ 3.9929221 sec
RG 32
DW 52.000 usec
DE 6.00 usec
TE 298.0 K
D1 4.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 8.00 usec

F2 - Processing parameters
SI 65536
SF 600.1300445 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 30.00 cm
F1P 9.000 ppm
F1 5401.17 Hz
F2P -0.500 ppm
F2 -300.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 250.05420 Hz/cm

ppm



```
Current Data Parameters
USER          taylor
NAME          BLT-2-053-A
EXPNO         3
PROCNO        1
```

```

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Date_          20090804
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PROBHD         5 mm TBI 1H/13
PULPROG        zg30
TD             9738
SOLVENT        CDCl3
NS             16
DS             2
SWH            9615.385 Hz
FIDRES         0.098178 Hz
AQ            5.0928259 sec
RG            228
DW            52.000 usec
DE            6.00 usec
TE            298.0 K
D1            0.10000000 sec
TD0           1

```

```
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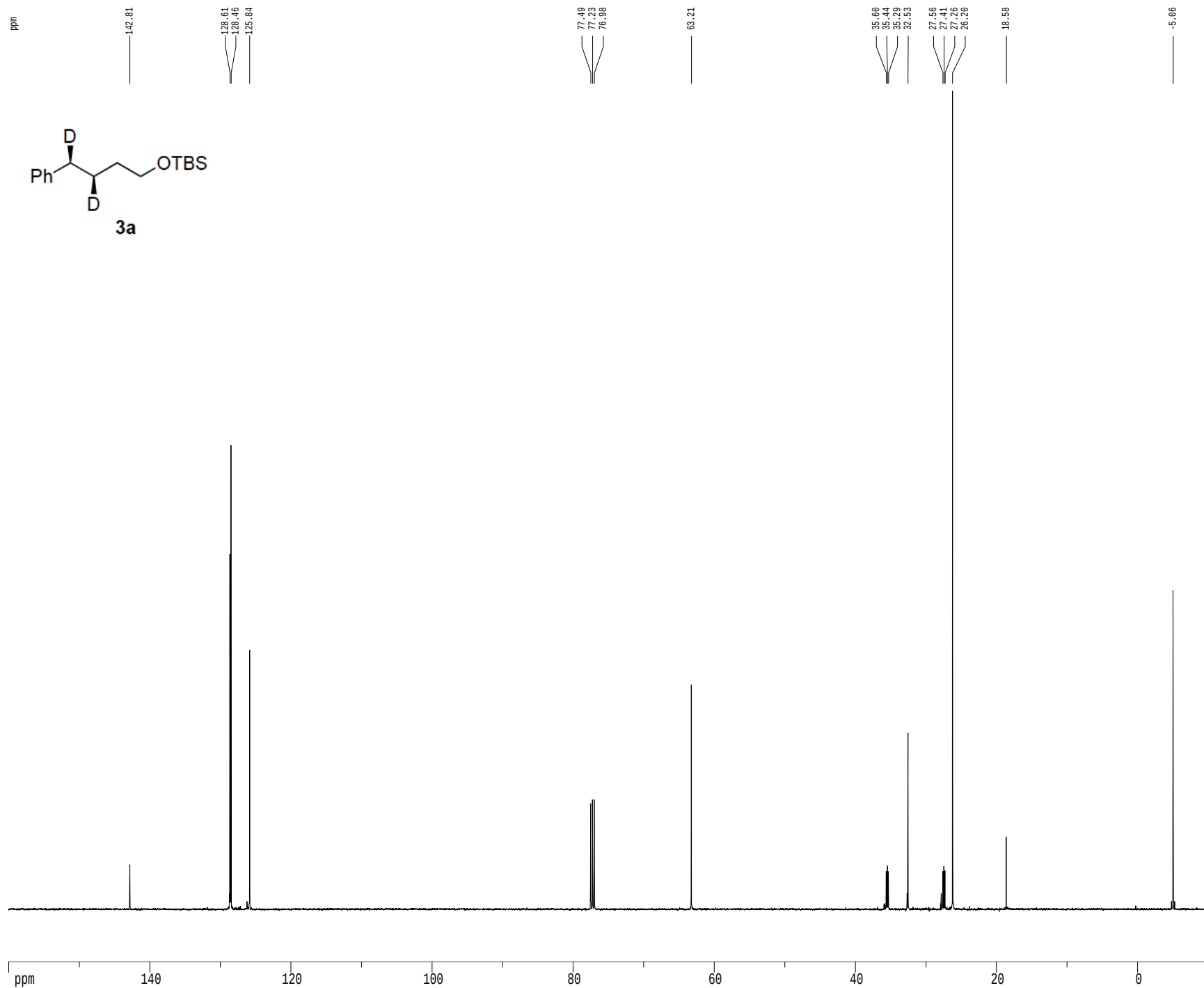
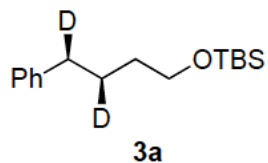
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WDW               EM
SSB               0
LB                0.30 Hz
GB                0
PC                1.00
```

```

1D NMR plot parameters
CX          22.80 cm
CY          30.00 cm
F1P         9.000 ppm
F1          5401.17 Hz
F2P        -0.500 ppm
F2        -300.06 Hz
PPMCM       0.41667 ppm/cm
HZCM       250.05420 Hz/cm

```

3a
syn-product
13C spectrum with 1H decoupling



Current Data Parameters
USER taylor
NAME BLT-2-053-A
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20090804
Time_ 18.41
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 314
DS 16
SWH 38383.831 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 7298.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 29.70 usec

===== CHANNEL f1 =====
NUC1 13C
P1 14.85 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SF01 125.7942548 MHz
SP1 3.60 dB
SP2 3.60 dB
SPNAM1 Crp60, 0.5, 20.1
SPNAM2 Crp60comp, 4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

===== CHANNEL f2 =====
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NUC2 1H
PCPD2 100.00 usec
PL2 1.00 dB
PL12 24.60 dB
SF02 500.2225011 MHz

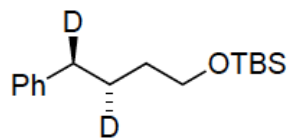
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GPY1 0.00 %
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GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804020 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.00 cm
CY 15.65 cm
F1P 160.000 ppm
F1 20124.87 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 7.45614 ppm/cm
HZCM 937.83636 Hz/cm

3b
anti-product
1H spectrum with 2H decoupling

ppm



3b

7.2795
7.2667
7.2542
7.2424
7.1797
7.1674
7.1548

3.6334
3.6227
3.6119

2.6849
2.5897

1.6608
1.6481
1.6347
1.6205
1.5667
1.5557
1.5441
1.5326

0.9851
0.8962
0.8698
0.7711

0.0872
0.0722
0.0628
0.0351
0.0086
-0.0845

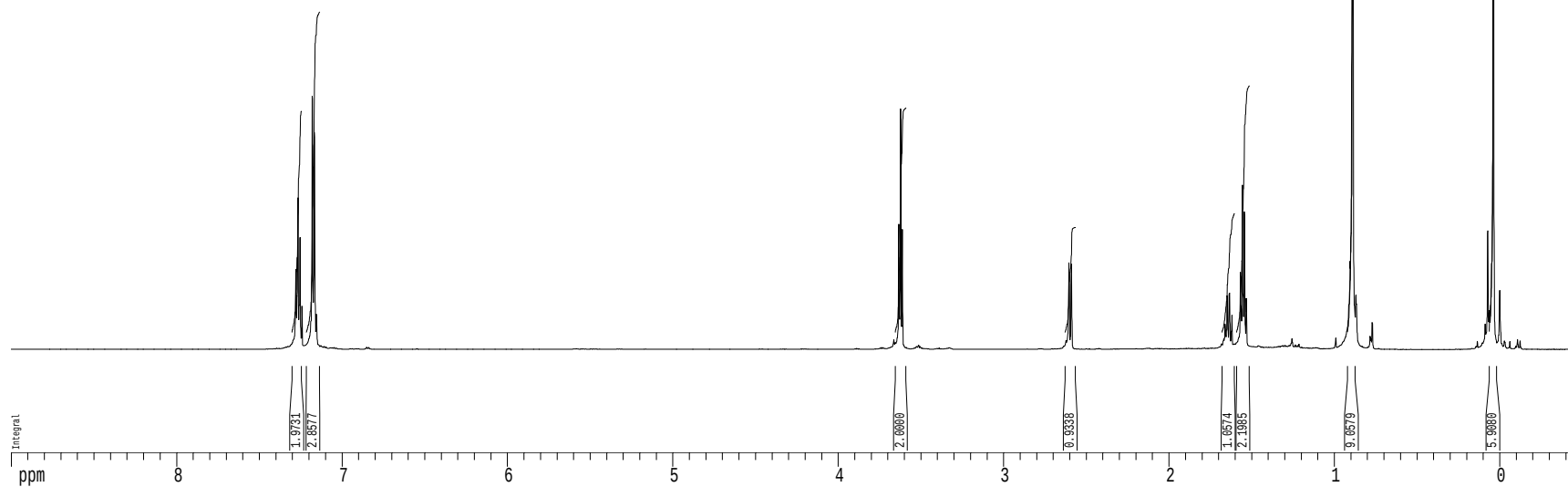
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EXPNO 27
PROCNO 1

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PULPROG zg1h2h.2
TD 76786
SOLVENT CDCl3
NS 8
DS 2
SWH 9615.385 Hz
FIDRES 0.125223 Hz
AQ 3.9929221 sec
RG 32
DW 52.000 usec
DE 6.00 usec
TE 298.2 K
D1 4.00000000 sec
D11 0.83000000 sec
D12 0.00002000 sec

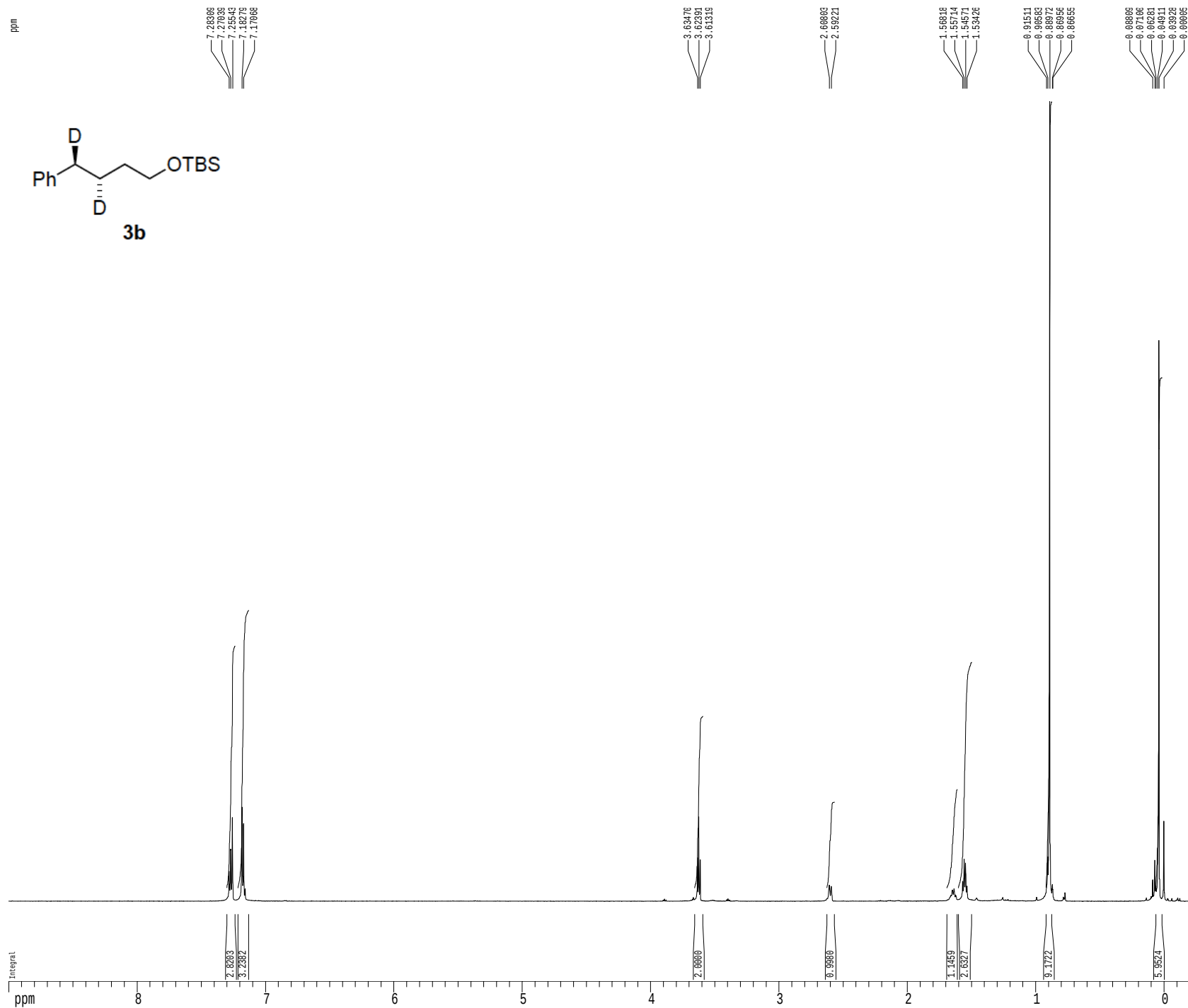
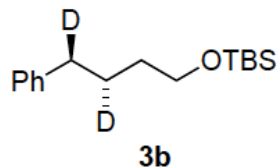
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NUC1 1H
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SF 600.1300463 MHz
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SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 30.00 cm
F1P 9.000 ppm
F1 5401.17 Hz
F2P -0.500 ppm
F2 -300.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 250.05420 Hz/cm



ppm



```
Current Data Parameters
USER          taylor
NAME          BLT-2-090-A
EXPNO         14
PROCNO        1
```

```

F2 - Acquisition Parameters
Date_          20110421
Time           12.87
INSTRUM        av6000
PROBHD         5 mm TBI 1H/13
PULPROG        zg30
TD             97938
SOLVENT         CDCl3
NS             8
DS             2
SWH            9615.385 Hz
FIDRES         0.098178 Hz
AQ            5.0928259 sec
RG            812
DW            52.000 usec
DE            6.00 usec
TE            298.1 K
D1            0.10000000 sec

```

```
===== CHANNEL f1 =====
NUC1          1H
P1            8.00 usec
```

```
F2 - Processing parameters
SI          65536
SF          600.1300370 MHz
WDW          EM
SSB          0
LB          0.30 Hz
GB          0
PC          1.00
```

1D NMR plot parameters	
CX	22.80 cm
CY	15.00 cm
F1P	9.000 ppm
F1	5401.17 Hz
F2P	-0.500 ppm
F2	-300.06 Hz
PPMCM	0.41667 ppm/cm
HZCM	250.95420 Hz/cm

Chemical structure of **3b** is shown in the top left corner. The structure is a 1-phenyl-3-(trimethylsilyloxy)propane-2,3-d₂, where the chiral center is labeled with a D (deuterium) atom. The structure is labeled **3b**.

The ¹³C NMR spectrum (400 MHz, CDCl₃) shows the following peaks (ppm):

- 142.83
- 128.62
- 128.46
- 125.84
- 77.48
- 77.23
- 76.96
- 63.23
- 35.59
- 35.44
- 35.29
- 32.54
- 27.56
- 27.41
- 27.25
- 26.26
- 18.59
- 5.06

The spectrum displays a series of peaks corresponding to the chemical structure, with the CDCl₃ solvent triplet centered around 77 ppm. The x-axis is labeled ppm and ranges from 0 to 140.

```

F2 - Acquisition Parameters
Date_          20110421
Time           12.24
INSTRUM        cryo500
PROBHD         5 mm CPTCI 1H-
PULPROG        SpinEcho309g.prd
TD             65536
SOLVENT        CDCl3
NS             1024
DS             16
SWH            3093.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG            7298.2
DW            16.500 usec
DE            6.00 usec
TE            298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D2            0.00200000 sec
d17           0.00019000 sec
M18           0.00000000 sec
MCKWRK        0.01500000 sec
P2            31.00 usec

```

```

===== CHANNEL f1 =====
NUC1                13C
P1                  15.50 usec
P11                 500.00 usec
P12                 2000.00 usec
PL0                  120.00 dB
PL1                  -1.00 dB
SF01                125.7942548 MHz
SP1                  3.20 dB
SP2                  3.20 dB
SPNAM1              Crp60, 0.5, 20.1
SPNAM2              Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

```

```
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CPDPRG2      waltz16
NUC2          1H
PCPD2        100.00 usec
PL2           1.60 dB
PL12          24.60 dB
SF02         500.2225011 MHz
```

```
===== GRADIENT CHANNEL =====
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GPNAM2          SINE.100
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GPX2             0.00 %
GPY1             0.00 %
GPY2             0.00 %
GPZ1             30.00 %
GPZ2             50.00 %
p15              500.00 usec
p16             1000.00 usec
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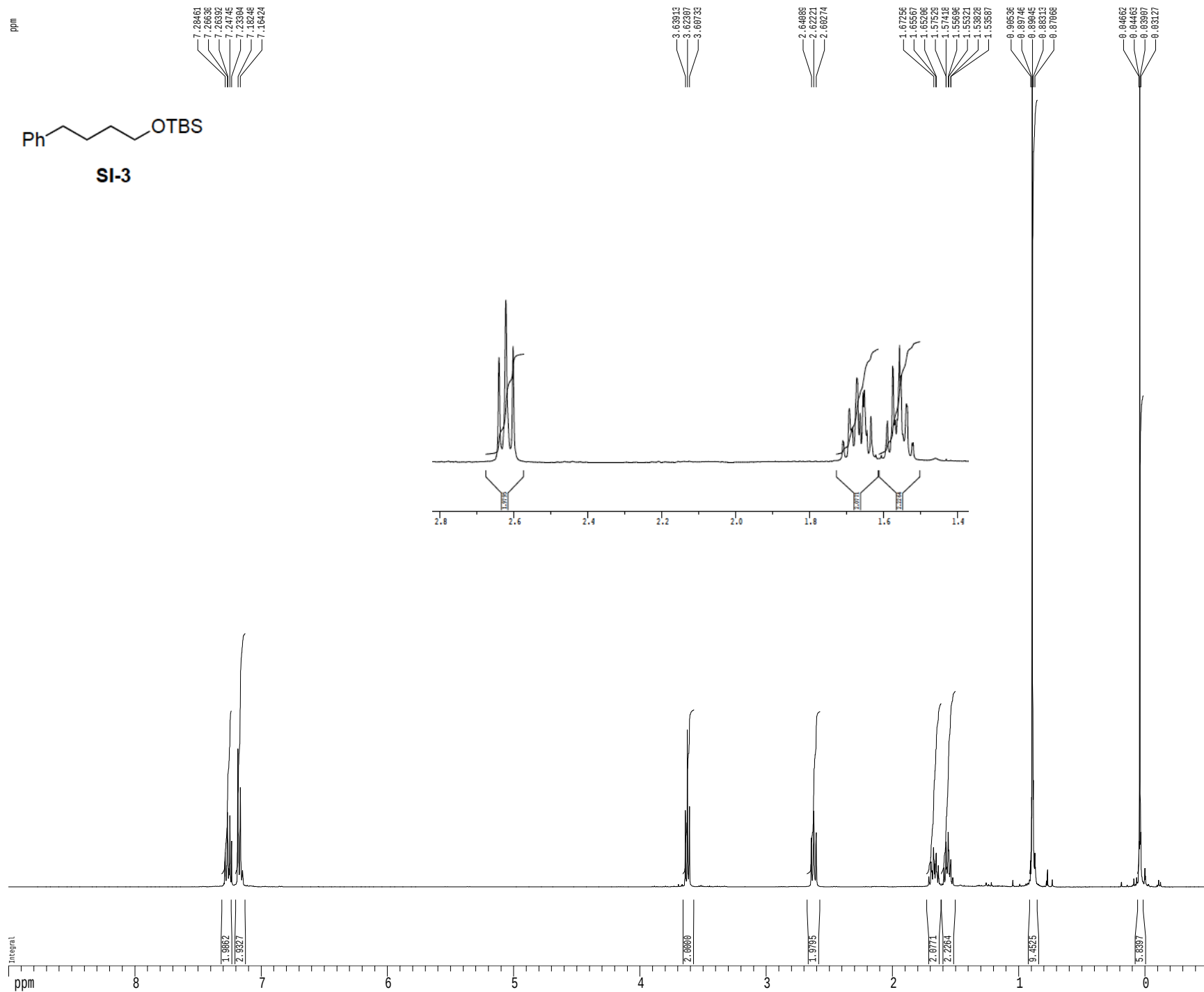
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SSB         0
LB          1.00 Hz
GB          0
PC          2.00
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1D NMR plot parameters
CX          22.80 cm
CY          15.65 cm
F1P         160.000 ppm
F1          20124.86 Hz
F2P         -10.000 ppm
F2          -1257.80 Hz
PPMCM       7.45614 ppm/cm
HZCM        937.83630 Hz/cm

```

SI-3
unlabeled product
1H spectrum



Current Data Parameters
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EXPNO 1
PROCNO 1

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Time 18.18
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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 64
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
SF01 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300324 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.00 cm
CY 30.00 cm
F1P 9.000 ppm
F1 3691.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm